

Nitrogen enriched solid sorbents for CO₂ capture

C. Pevida, M.G. Plaza, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis

Department of Energy and Environment, Instituto Nacional del Carbón (CSIC), Apartado 73,
33080 Oviedo, Spain

Email: frubiera@incar.csic.es

Abstract

Reducing anthropogenic CO₂ emissions to slow down the consequences of climate change concerns all developed countries. In the short term, one of the most viable options to cut down carbon emissions consists on CO₂ capture and storage from large stationary sources such as power stations, cement plants, refineries, etc. The near-ready-to-use technology at this scale is amine scrubbing. However, it is still necessary to reduce the cost of the capture step. Adsorption with solid sorbents is one of the promising options. In this work, a series of materials obtained from a commercial activated carbon were evaluated as potential high capacity carbon dioxide adsorbents. Functionalisation of the parent carbon by heat treatment with gaseous ammonia was carried out in order to introduce nitrogen functionalities of basic character to the carbon structure. The aim was to improve the selectivity and capacity of the sorbents towards CO₂ capture. The sorbents were characterised in terms of texture, chemical composition, and surface chemistry. The textural characterisation involved N₂ and CO₂ adsorption isotherms at -196 °C and 0 °C, respectively. The surface chemistry was studied through temperature programmed desorption analysis in a thermobalance coupled to an FTIR for the evolved gas analysis. The capture performance of the sorbents was evaluated by means of a thermogravimetric analyser, recording the mass uptake of the samples when exposed to a CO₂ atmosphere.

Keywords

CO₂ capture, adsorption, carbon materials

INTRODUCTION

The international community's growing awareness on climate change, evidence an urgent need for the worldwide implementation of technologies designed to reduce greenhouse gas emissions. The growth in energy demand makes it impossible to reduce in the near time the use of fossil fuels, which constitute the main sources of greenhouse gas emissions. In the short term, one of the most viable options to cut down carbon emissions consists on CO₂ capture and storage from large stationary sources such as power stations, cement plants, refineries, etc.

Current or proposed methods of CO₂ capture from flue gas include absorption, adsorption, cryogenic distillation and membrane separation. Adsorption is considered one of the most appealing options for CO₂ capture purposes. However, efficient capture of CO₂ using adsorption requires solid adsorbents with high CO₂ selectivity and capacity. The development of a new generation of materials that would efficiently adsorb CO₂, will undoubtedly enhance competitiveness of adsorptive separation in a flue gas application.

Porous materials, such as molecular sieves and zeolites, as well as activated carbons, are suitable materials for CO₂ capture by adsorption with solid sorbents due to their developed porous structure [Xu, 2002; Siriwardane, 2005]. Activated carbons, particularly, present highly developed micro and mesoporosity which is applied in a wide range of industrial and technological processes [Bansal, 1998].

The adsorption properties of a solid sorbent are controlled by its porous structure and surface chemistry. It has been shown that the CO₂ adsorption capacity of activated carbons -that is governed by physical adsorption- can be increased introducing nitrogen functional groups to

its structure [Huang, 2003; Gray, 2004; Przepiorski, 2003; Maroto-Valer, 2005; Arenillas, 2005; Drage, 2007]. Increasing basicity can be mainly achieved through two techniques: impregnation with proper chemicals or heat treatment with gaseous ammonia. Impregnation has been frequently used although blocking of the porous structure could take place, lowering the adsorption capacity of the activated carbon. Thus, in this work a commercial granular activated carbon has been modified by treatment with gaseous ammonia at different temperatures. Ammonia decomposes at high temperatures with the formation of radicals, such as NH_2 , NH and H . Those radicals may react with the carbon surface to form functional groups, such as $-\text{NH}_2$ -, $-\text{CN}$, pyridinic, pyrrolic, and quaternary nitrogen [Boehm, 1984].

EXPERIMENTAL

A commercial granular activated carbon supplied by Norit -here referred to as C- has been chosen as starting material for the preparation of CO_2 capture adsorbents. It is a wood-based carbon manufactured by a phosphoric acid activation process.

Ammonia Heat Treatment

In this work, treatment of activated carbon C with gaseous ammonia at different temperatures has been carried out in a vertical furnace. Around 3 g of C -dried overnight at 100°C - were placed in a quartz reactor and held under 50 mL min^{-1} of N_2 flow rate for 30 min. When the furnace reached the desired temperature -values between 600 and 900°C - the quartz reactor was introduced in the furnace. Once the sample reached the furnace temperature the flow was changed from N_2 to ammonia (50 mL min^{-1}) and held for 2 h. Then, the sample was removed from the furnace and cooled to 100°C under ammonia flow. Finally the flow was changed to N_2 until room temperature was reached. The modified carbons were denoted as CN followed by the temperature used in the treatment with ammonia, i.e. CN600.

Chemical and textural characterization of the samples

Ultimate analysis was carried out in order to determine the extent of nitrogen incorporation to the carbons. The acid-basic character of the samples was estimated by means of the Point of Zero Charge (pH_{PZC}); a mass titration method adapted from Noh and Schwarz was used for that purpose [Noh, 1988]. Helium density was measured in an Accupyc 1330 at 35°C . Adsorption isotherms of N_2 at -196°C and CO_2 at 0°C , were carried out in a Micromeritics Tristar 3000. Samples were outgassed at 100°C under vacuum for 24 h prior to density and adsorption measurements. The apparent surface areas were calculated from the physical adsorption of N_2 using the BET equation in the linear form proposed by Parra et al. [Parra, 1995] and the total pore volumes were evaluated using the Gurvitch's rule ($p/p^0 = 0.99$). The mesopore volume comprises pores between 2 and 50 nm according to IUPAC classification [Olivier, 1998]. They were calculated by the DFT method applied to the N_2 isotherms, assuming slit shape pores and non-regularisation [Seaton, 1989]. The micropore volumes were calculated by the Dubinin-Radushkevich (DR) method [Dubinin, 1966], from the CO_2 adsorption isotherms (assuming an affinity coefficient of 0.36), and the average width of the micropore system by using the Stoeckli-Ballerini relation [Stoeckli, 1991].

Temperature-Programmed Desorption (TPD) tests

The ammonia-treated samples were subjected to TPD tests using a Setaram TGA 92 thermogravimetric analyser (TG) coupled to a Nicolet Nexus Fourier Transform Infrared (FTIR) spectrometer. 20 mg of sample was heated at $15^\circ\text{C min}^{-1}$ up to 1000°C under an Argon flow rate of 50 mL min^{-1} . The final temperature was maintained for 30 min. The evolved gases were transferred through a heated interface to the FTIR for analysis.

CO_2 adsorption capacity experiments

The CO_2 adsorption-desorption performance of the samples was evaluated in the TG analyser. The CO_2 adsorption capacity of the samples was determined from the mass uptake

registered when exposed to pure CO₂. Prior to the adsorption measurements, the samples were dried at 100°C in 50 mL min⁻¹ of Ar for 1h, and allowed to cool to 25 °C. Afterwards Ar was changed to 50 mL min⁻¹ of CO₂ and the temperature was held at 25 °C for 1 h. Then, the temperature was increased at a heating rate of 0.5 °C min⁻¹ up to 100 °C, and the mass change was recorded, to evaluate the influence of temperature on CO₂ capture capacity. The sample was kept at 100 °C for 1 h and finally the flow was turned to Ar to regenerate the sample.

RESULTS AND DISCUSSION

The ultimate analysis and the pH_{PZC} of the parent carbon, C, and the ammonia-modified carbons, CN, are presented in Table 1. Ammonia treatment increases the nitrogen content up to 8 wt % for the carbon treated at 700 °C, CN700. With respect to temperature, the nitrogen content reaches a maximum at 700 °C and gently decreases at higher temperatures, most probably due to partial gasification of the carbon with ammonia at higher temperatures. Ammonia is thought to react with oxygenated functionalities in the carbon, which may be in agreement with the drastic reduction of the oxygen content observed for the carbons heat treated with ammonia. As expected, the acid character of carbon C changed to basic after heat treatment with gaseous ammonia.

Table 1. Chemical characteristic and yields of the carbon materials studied

Sample	Product yield (wt %)	Ultimate Analysis (wt %, db)				pH _{PZC}
		C	H	N	O	
C	100	82.9	3.0	0.4	13.7	2.8
CN600	87	91.2	1.7	3.5	3.6	7.8
CN700	86	86.6	1.0	8.1	4.3	8.8
CN800	74	88.7	0.7	6.3	4.3	8.9
CN900	54	91.6	0.6	4.6	3.2	9.1

Table 2. Textural parameters calculated for the studied samples

Sample	d _{He} (g cm ⁻³)	N ₂ adsorption at -196 °C			CO ₂ adsorption at 0 °C		
		S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	W ₀ (cm ³ g ⁻¹)	E ₀ (kJ mol ⁻¹)	L (nm)
C	1.51	1361	0.965	0.441	0.215	26.07	0.74
CN600	1.69	1095	0.749	0.329	0.198	27.96	0.65
CN700	1.87	1023	0.686	0.292	0.206	29.36	0.60
CN800	1.92	1190	0.831	0.354	0.221	28.97	0.61
CN900	2.06	1521	1.074	0.533	0.169	29.69	0.59

The textural parameters calculated from the N₂ isotherms at -196 °C and the CO₂ isotherms at 0 °C together with the He density, are presented in Table 2. All carbons studied are mainly microporous. Modification of carbon C by ammonia treatment results in lower BET apparent surface areas for the carbons modified at temperatures between 600 and 800 °C –CN600, CN700, CN800-. However, for the carbon modified at 900 °C a significant increase in S_{BET} is observed. Accordingly, the total pore (V_p) and mesopore (V_{meso}) volumes show the same trend. The micropore volume (W₀) slightly changes after reaction with ammonia at the

different temperatures. These results suggest that the ammonia treatment at temperatures below 700 °C partially block the mesopores in the parent carbon C. At higher temperatures, 900 °C, gasification of the carbon with ammonia promotes the development of mesoporosity. The thermal stability of N-containing groups, introduced into the carbon structure during heat treatment with ammonia, was assessed by means of TG-TPD-FTIR tests. The only nitrogen-containing compounds detected for the ammonia-modified carbons were NH₃ and HCN. As expected, for the parent carbon C no nitrogen compounds were detected. Figure 1 presents the NH₃ and HCN profiles analysed by FTIR for the modified carbons.

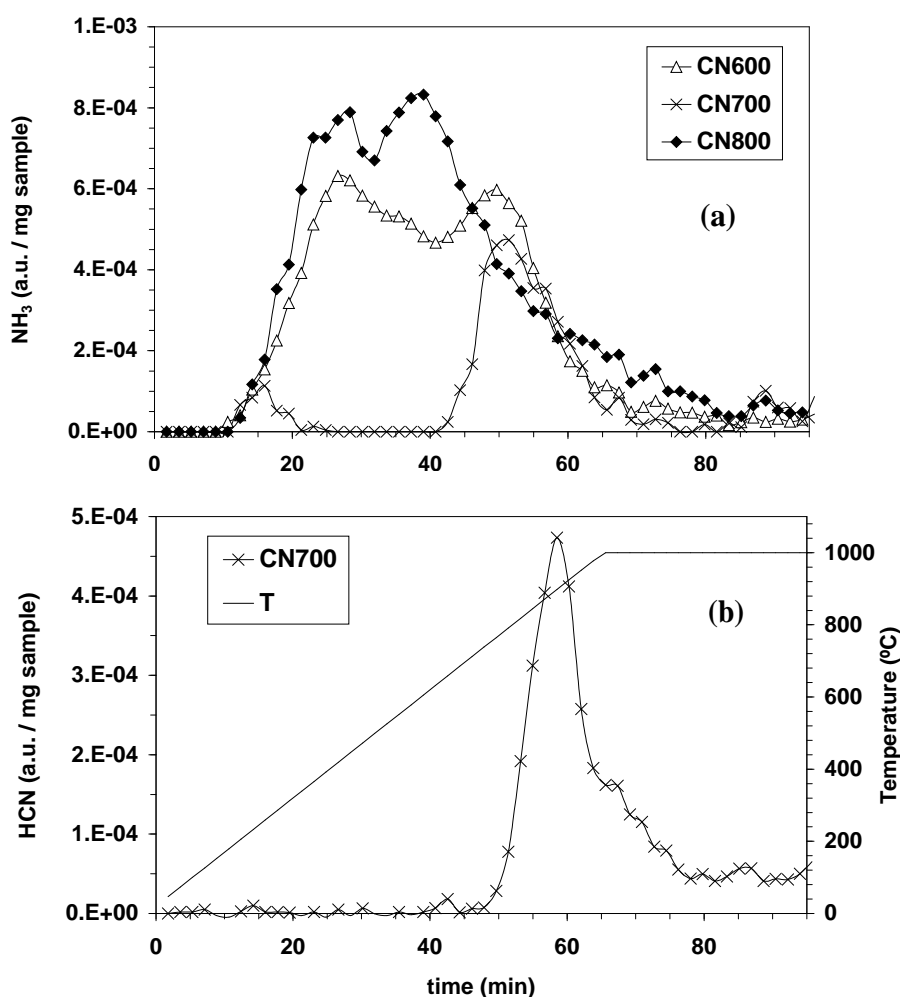


Figure 1. NH₃ (a) and HCN (b) profiles for the ammonia-modified samples during TPD tests.

Ammonia-modified samples show different NH₃ and HCN profiles depending on the temperature of the treatment they have undergone. This indicates that different nitrogen functionalities are introduced in the modified samples. CN800 shows the highest NH₃ intensities with two characteristic peaks at around 400 and 600 °C. HCN emission is absent for CN800. However, nitrogen functionalities in CN700 decompose into NH₃ –main peak at 800 °C– and HCN –peak at 900 °C–. CN600 profiles present an intermediate behaviour with two NH₃ characteristic peaks at 400 and 800 °C, and no HCN evolution. The results suggest that ammonia treatment at 600 °C would introduce nitrogen in at least two different types of functionalities. At 700 °C nitrogen would be ascribed to thermally more stable nitrogen functionalities. Increasing temperature would thermally stabilise the nitrogen introduced. However, at 800 °C and above, less nitrogen is incorporated probably due to the effect of carbon gasification with ammonia. At 800 °C part of this nitrogen would be ascribed to more

labile compounds that evolve as NH_3 , but at higher temperatures $\sim 900^\circ\text{C}$ it is most probably introduced and stabilised into aromatic rings that do not decompose during the TPD tests.

Mass uptakes during the non isothermal CO_2 adsorption tests for the carbons studied are shown in Figure 2. Mass uptakes are expressed in g CO_2 adsorbed per 100 g of dried sample. For all the studied samples the highest capacities are achieved at room temperature; it can be seen in Figure 2 that the increase in temperature is accompanied by a decrease in CO_2 uptake. Maxima adsorption capacities at 25 and 100°C are summarised in Table 3.

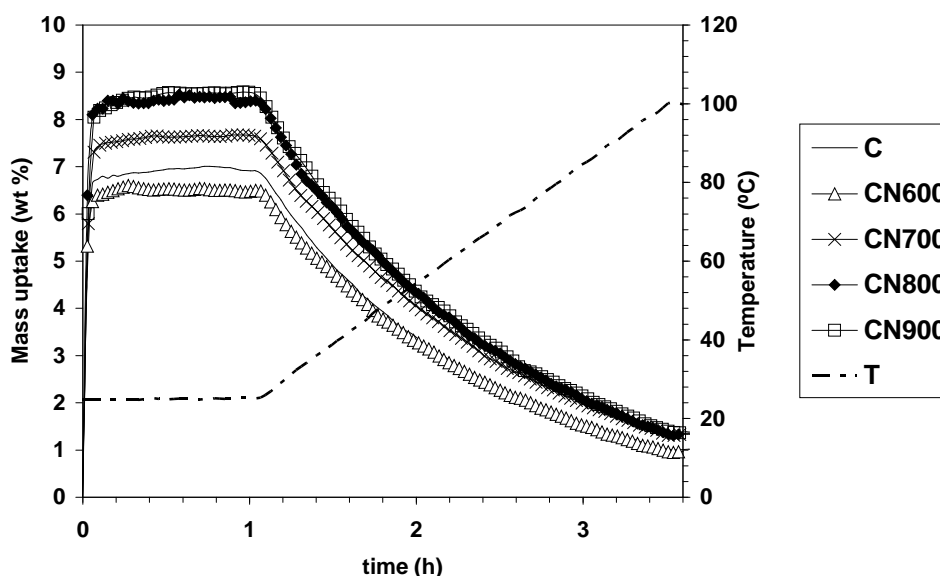


Figure 2. Temperature-programmed CO_2 adsorption tests for the studied carbons.

Ammonia-modified carbons heat-treated at temperatures of 700°C and above present higher adsorption capacities than the parent carbon C. Differences in CO_2 capture capacity between the parent carbon C and the ammonia heat-treated carbons being more significant at 25°C than at 100°C . CO_2 physisorption is the mechanism governing CO_2 capture on carbon C. Introducing nitrogen-functionalities by ammonia treatment at different temperatures intends to enhance the CO_2 capture performance adding the increasing effect of a suitable chemistry. This seems to happen for the carbons modified at $T \geq 700^\circ\text{C}$. However, for the carbon modified at 600°C a decrease in CO_2 capture capacity with respect to carbon C is observed. Although there is a 3.5 % of nitrogen in CN600, it does not enhance its capture capacity. The textural characteristics of CN600 seem to be controlling its CO_2 capture performance. This may be due to the ineffectiveness of the nitrogen functionalities incorporated by the ammonia treatment at 600°C or to the fact that the effect of these functionalities cannot compensate the decrease in the textural properties of CN600 with respect to the parent carbon C. Further research to identify the type of nitrogen functionalities active towards CO_2 capture is being carried out.

Table 3. CO_2 adsorption capacities at 25 and 100°C

CO_2 adsorption capacities (wt. %)	C	CN600	CN700	CN800	CN900
25°C	7.0	6.5	7.7	8.5	8.6
100°C	1.0	1.0	1.3	1.3	1.4

CONCLUSIONS

A commercial granular activated carbon supplied by Norit has been modified by gaseous ammonia heat treatment at different temperatures (600-900 °C). This treatment has effectively introduced nitrogen into the structure of the carbons, thus giving them a basic character. TPD tests revealed that depending on the temperature of the ammonia treatment, the nitrogen-functionalities introduced were different. CO₂ capture capacities of the ammonia heat treated carbons at temperatures of 700 °C and above were enhanced by the presence of nitrogen functionalities, whereas for the sample modified at 600°C the nitrogen seem to be ineffective towards CO₂ capture.

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